

# METHOD OF MAKING A CERAMIC BODY OF DENSIFIED TUNGSTEN CARBIDE

## RELATED APPLICATIONS

This application claims priority to US Provisional Patent Application (20264-502 (Cerb-2)), filed November 6, 2001, express mail label EL585246941US. The contents of this application are incorporated by reference in its entirety.

## FIELD OF THE INVENTION

The present invention relates to ceramic bodies comprised of polycrystalline tungsten carbide metal, the method of making these ceramic bodies, and the ceramic material of which the bodies are made.

## BACKGROUND OF THE INVENTION

It took metallurgists one hundred and fifty years after Scheele's discovery of "tungsten" in 1781, to develop and then apply tungsten carbide ("WC") cermets in industry. Cermets are a composite material consisting of a combination of metallic and ceramic materials. The most common cermets are the cemented carbides, composed of an extremely hard ceramic (*e.g.*, WC, TiC), bonded together by a ductile metal such as cobalt or nickel. Many different types of polycrystalline WC-based metal powders (*e.g.*, U.S. Patent Nos. 4,664,899; 5,746,803; 6,007,598) and composites (*e.g.*, U.S. Patent Nos. 4,828,584; 5,563,107; 5,612,264; 5,681,783; 6,033,789) have been described.

Today, the main use of tungsten (in the form of WC) is in the manufacture of cemented carbide. Due to the wide application of cemented carbide products in engineering, electronics, mining, manufacturing, aerospace, and medicine, the annual world market demand for cemented carbide now exceeds some 30,000 tons. In manufacturing, for example, durable and effective

cutting tools for high-speed machining have significant commercial applications. The material comprising these cutting tools should have a high heat hardness, a high transverse rupture strength, and fracture toughness. Further, these cutting tools are designed to control the flow of "chips" which are formed in the machining process, and, to reduce the cutting forces.

5 Polycrystalline WC-based cermets have shown two fundamental limitations. Under certain conditions, WC-based cermets lack toughness (*i.e.*, they are brittle in response to mechanical shock), and at the high temperatures caused by faster feed rates, they undergo plastic deformation. Polycrystalline WC is, therefore, disfavored in the preparation of densified ceramic bodies for select applications (*e.g.*, cutting tool inserts with chip control) because WC is not  
10 thought to have the needed toughness and wear resistance.

In general, hardness of the cermets, *i.e.*, wear resistance, strength, and toughness, can be changed by WC grain size, cobalt content, and by other carbides present. In formulating these materials, however, there is a tendency that if wear resistance is heightened, fracture resistance is lowered. Conversely, if fracture resistance is heightened, wear resistance is lowered.  
15 Accordingly, in the design of densified polycrystalline WC-containing ceramic bodies, it has been a challenge to improve one material property without adversely affecting another material property by adding cobalt, or another iron group, that will plastically deform in high heat, *e.g.*, high-speed machining.

## SUMMARY OF THE INVENTION

### 20 TUNGSTEN CARBIDE POWDER AND METHOD OF MAKING

A method of producing a WC powder is included in the present invention. In one embodiment, the method of producing the WC powder comprises mixing tungsten particles with carbon powder; ball milling the mixture; adding a grain growth inhibitor; transferring the milled mixture to a refractory crucible; and carburizing the mixture under conditions sufficient to create  
25 WC particles.

In one embodiment, the initial tungsten particles are selected from a group consisting of metatungstate, pertungstate, and tungstic acid. Preferably, the mixture comprises 94 parts by percent tungsten and 6 parts by percent carbon. Typically, the powder is produced by milling the

mixture for at least about 20 h. Vanadium carbide or chromium carbide, or a combination of vanadium carbide and chromium carbide are typically used as a grain growth inhibitor, preferably vanadium carbide is used as a grain growth inhibitor. While the grain growth inhibitor may be added after the milling process, preferably the grain growth inhibitor is added before the milling process is complete. The milled powder is heated to between about 1475° C and about 1700° C (preferably 1600° C) in an atmosphere suitable to yield formation of WC particles.

In one embodiment, the method of producing a WC powder yields a powder comprising fine-grained WC and less than about 6.09 weight percent ("wt %") carbon (*i.e.*, substoichiometric) and less than 0.6 wt % cobalt. Preferably, the average diameter of the manufactured WC grains is less than about 5 µm. In a preferred embodiment, WC grains between about 0.1 µm and about 0.75 µm are preferred. The WC powder may be used to form densified ceramic bodies of surprisingly high transverse rupture strength that exceeds about 300,000 psi as described below.

#### **DENSIFIED CERAMIC BODY AND METHOD OF MAKING**

This invention provides densified ceramic bodies composed of essentially dense, fine-grained WC. The invention also provides a method that yields a WC-containing ceramic body with sub-micron metal grains and a surprisingly high transverse rupture strength that exceeds about 300,000 psi. The densified ceramic bodies described herein may be formed into a variety of shapes including cutting tools, inserts, router bits and knives.

In one embodiment, the method of manufacturing the densified ceramic bodies comprises milling a WC powder with a suitable organic solvent for more than 71 h, such that rough edges on the particles in the powder are reduced during the process, cobalt is added to the milling mixture relatively early in the milling process (preferably in the first 5% to 10% onto the total milling time) to swedge cobalt onto the particles in the powder. The milled powder and solvent slurry is then contacted with a mixture comprising paraffin-type wax and an ester-type wax and granulated into substantially spherical granules of WC particles and said paraffin-type and ester-type wax. The granulated powder is then compacted under conditions sufficient to form a preform ceramic body having 40% to 60% density of pure WC. Subsequently, the paraffin-type

wax and ester-type wax are removed from the preform ceramic body at elevated temperature, thereby forming a debindered population of WC particles. Finally, the debindered preform ceramic body is sintered to form a densified WC-containing body. Debinding and sintering may be accomplished in a single cycle.

5 In another embodiment, a densified ceramic body is made by ceramic processing techniques that result in a ceramic body which has a density of greater than 95 wt % of its theoretical density with substantially all grains having an average size of 0.001  $\mu\text{m}$  to 0.6  $\mu\text{m}$  and a transverse rupture strength of at least about 300,000 psi. Preferably, the densified ceramic body has a transverse rupture strength of at least about 300,000 psi, a Rockwell A-scale hardness of up to about about 96 at 20° C (preferably between about 95 and about 96 at 20° C) and a Rockwell A-scale hardness of greater than 90 at 800° C. The densified ceramic body has cobalt present from about 0.01 wt % to about 1 wt % (preferably less than about 0.6 wt %) and includes at least 98 wt % WC. Further, the average WC particle size is less than about 1.0  $\mu\text{m}$  (preferably between about 0.001  $\mu\text{m}$  and about 0.6  $\mu\text{m}$ ). Tungsten-bound carbon is present in at least about 5.5 wt % and the ceramic body has a density of at least about 95 wt % of its theoretical density (preferably 99% of its theoretical density).

15 The polycrystalline fine-grained WC ceramic material of this invention is useful in applications where a tough, wear-resistant material is required, *e.g.*, bearings, balls, valve seats, pistons, and mill liners; in applications where a non-brittle high density material is required, *e.g.*, for counterweights in aircraft, for darts, or for weights in golf club heads; and, it is also useful in armament applications, *e.g.*, as high velocity penetrators in anti-tank weapons.

20 The densified ceramic bodies of this invention are particularly useful as wear parts in high-speed manufacture techniques using various cutting tools, *e.g.*, drills; Reuters; taps; milling cutters; gear cutters; saw blades, as well as for punches and dies. These densified ceramic bodies may be used to machine a wide variety of materials, including the machining of titanium metals and alloys of titanium which have a very high content of titanium, cast iron, aluminum, high nickel alloys, stainless steels, wood machining-cutting, and high-speed machining of steels.

## DETAILED DESCRIPTION OF THE INVENTION

### TUNGSTEN CARBIDE POWDER AND METHOD OF MAKING

The present invention provides for a method of manufacturing a tungsten carbide powder that contains carbon at less than about 6.09 wt %; cobalt at less than about 0.6 wt %; and a grain growth inhibitor selected from a group consisting of vanadium carbide, chromium carbide, titanium carbide, tantalum carbide, and molybdenum carbide. A ceramic powder is made by ball-milling a mixture of tungsten particles and carbon powder. A grain growth inhibitor is added during the ball-milling process or thereafter. The milled powder is subsequently transferred to a refractory crucible and carburized to form WC particles. The initial tungsten powder may be selected from a group consisting of metatungstate, pertungstate, and tungstic acid, and the grain growth inhibitor may be added as metals or oxides which may be co-carburized with the WC.

Carbon powder is added to the tungsten carbide powder to less than 6.13 wt % (*i.e.*, substoichiometric) or in an amount that produces a final composition after processing that is substoichiometric in carbon. The mixture may be comprised of 94 parts by percent tungsten and 6 parts by percent carbon but a carbon powder to between 5.9 wt % and 6.09 wt % is preferred. Cobalt is added to less than 0.6 wt % but cobalt at a final concentration to between 0.25 wt % and 0.5 wt % is preferred. Either chromium carbide or vanadium carbide or a combination of chromium carbide and vanadium carbide may be used as the grain growth inhibitor, however, vanadium is the preferred grain growth inhibitor. The milling of the powder is conducted for at least about 20 h.

Carburization may be obtained by heating the metal mixture in a refractory crucible under nonreducing conditions in a suitable furnace to temperatures exceeding 800° C. Heating the metal mixture to between 1425° C and 1700° C is preferred. Heating the metal mixture to 1600° C is most preferred. Any nonreducing conditions suited to the carburization of tungsten may be used. A nonreducing environment of nitrogen in the absence of vacuum is preferred.

The average diameter of the WC ceramic particles in the manufactured ceramic powder may be 5  $\mu\text{m}$  or less. The ceramic grains between about 0.1  $\mu\text{m}$  and about 0.75  $\mu\text{m}$  are preferred. The WC powder may be used to form densified ceramic bodies of surprisingly high transverse rupture strength that exceeds about 300,000 psi as described below.

## DENSIFIED CERAMIC BODY AND METHOD OF MAKING

The present invention provides for a densified ceramic body with a transverse rupture strength exceeding about 300,000 psi and molded from WC powder. The ceramic body may be shaped as a cutting tool, router bit, knife or insert. Preferably the densified ceramic body is a ceramic cutting tool. More preferred is a ceramic cutting tool for high-speed machining that includes a cutting edge, a rake face with a chip control groove surface, a flank face and the cutting edge that is formed at the juncture of the flank face and the rake face. The ceramic body may be used to cut metal or wood.

The invention provides that a densified ceramic body be formed by milling a population of WC particles with organic solvent and milling balls under conditions sufficient to reduce the rough edges on particles in the powder and to swedge (*i.e.*, bond by pounding) 0.3 wt % to 0.35 wt % cobalt onto the particles in the powder; contacting the population of granulated WC particles with a mixture comprising a paraffin-type wax and an ester-type wax; spraying the resulting mixture via a nozzle into a gas filled vessel under conditions sufficient to remove the organic solvent and leave spherical granules of said paraffin-type and ester-type wax containing WC particles; molding said granule material into a preform body; then removing said paraffin-type wax and ester-type wax from said preform body, thereby forming a debindered population of WC particles; and then sintering said debindered population of WC particles, thereby forming a densified WC-containing ceramic body with 0.26 wt % to 0.6 wt % cobalt.

Tungsten carbide ceramics of the present invention can be tailored for use in particular applications by an appropriate milling of the WC powder to reduced grain size and by controlling densification conditions to control grain growth. Desirable starting powder grain sizes fall within a range of from greater than 0.001  $\mu\text{m}$  to about 5  $\mu\text{m}$ . The range, depending on the application, is preferably from about 0.1  $\mu\text{m}$  and about 0.75  $\mu\text{m}$ . Starting powder grain sizes of less than 5  $\mu\text{m}$  provide densified ceramic bodies having excellent properties.

Tungsten carbide powders having an average grain size of less than or equal to 5  $\mu\text{m}$  are commercially available (Alldyne Powder Technology, West Huntsville, AL, USA). One such powder, Mach 600, has a nominal average grain size of 0.8  $\mu\text{m}$  to 1.1  $\mu\text{m}$  and includes a small

amount of vanadium carbide as a grain growth inhibitor. Attriting such a powder simultaneously reduces the average grain size, reduces grain size distribution, and more uniformly disperses the grain growth inhibitor. Even in the absence of a grain growth inhibitor, attrition/milling provides the benefits of smaller average particle size and a narrower particle size distribution.

5 Processing of a WC powder to the desired particle distribution and shape may entail repeated cycles of ball-milling the WC powder with organic solvent and mill-balls followed by spray-drying. The range, depending on the application, is preferably from about 71h total milling time to more than about 400-h of total milling time. A milling time between about 150 h and about 350 h is preferred. A milling time of between about 220 to about 240 h is most preferred.

10 Cobalt is added to the milling mixture at between about 5% and about 10% into the total milling time to swedge cobalt onto the WC particles in the powder. Further, any organic solvent compatible with the milling of WC powder, *e.g.*, n-heptane, may be used to ball-mill the WC powder to a reduced grain size. The use of n-heptane is preferred. Following milling, the WC powder is thrown into the air under conditions sufficient to granulate the WC particles into a spherical shape.

15 Alternatively, the WC powder may have these characteristics as synthesized. As a further alternative, powders with even larger average grain sizes may be used provided they are attrited/milled under conditions sufficient to reduce the average grain size to less than or equal to about 0.6  $\mu\text{m}$ . These powders necessarily require longer size reduction procedures and may, as a consequence, pick up additional quantities of impurities from media used to promote size reduction.

20 Tungsten powders used in the present invention need not be 100% pure. They may contain other materials, *e.g.*, less than 2 wt %, of other materials so long as the other materials do not interfere with densification of the powder or adversely affect physical properties of the resultant densified ceramic bodies. Examples of "other materials" include cobalt, iron, nickel, carbon and silicon. The other materials may, for example, be present as a result of powder synthesis procedures or as residue from milling operations. In some embodiments, carbon-bound tungsten content is greater than 5.9 wt %. Preferably, the carbon content is sub-stoichiometric.

Cobalt may be present from about 0.01 wt % to about 1 wt %. Preferably, cobalt is present at less than 0.6 wt %. In addition to the other materials, the WC powders have an oxygen content that varies inversely with particle size. Thus, as particle size decreases, oxygen contents tend to increase. However, the oxygen content should be maintained at a level that does not interfere with densification of the powder or adversely affect physical properties of resultant densified ceramic bodies.

In another aspect of the present invention, sintering of the preform ceramic body is accomplished under vacuum and the temperature is increased at a rate of at least about 6° C per minute to at least about 1580° C and maintained at this temperature for at least about 45 min, and at least about 28 KSI inert gas pressure is applied and held for at least about 45 min. In yet another aspect, the inert gas is selected from a group consisting of nitrogen, argon, helium, neon, krypton, and xenon.

After the milling process, the attrited WC powder is bound together, preferably with wax or a mix of waxes as described more fully below. More specifically, a binder such as wax is added to the powder to facilitate molding into a die. Preferably, the total binder content of the WC powder is less than about 5 wt %. More preferably the total binder content of the WC powder is about 2.25 wt %. The binder may contain a mixture of paraffin-type and ester-type waxes. A paraffin-type wax is a hydrocarbon that consists of saturated straight, branched and/or cyclic hydrocarbon chains. Paraffin-type wax based on mineral oil may contain about 20 to 50 carbon atoms whereas other, particularly synthetic, paraffin-type waxes, may contain up to 100 carbon atoms. Paraffin-type waxes include, *e.g.*, petroleum wax such as solid paraffin or microcrystalline wax, a hydrocarbon wax such as liquid paraffin or white soft paraffin. On the other hand, ester-type waxes, as defined here, are essentially esters in chemical structure and may be found in naturally occurring mixtures. Ester-type waxes include, however, synthetic or partially synthetic waxes or mixtures of waxes based on naturally occurring ester-type waxes.

Preferably, beeswax, montan wax, carnauba wax, and spermaceti is selected as the ester-type wax. More preferable, beeswax is selected as the ester-type wax. It is also preferable to add the paraffin-type to greater than 0.1 wt % WC powder and to add the ester-type wax to less than approximately 5 wt % WC powder. In one embodiment, paraffin-type is added to 2 wt % of the



WC powder and beeswax is added to 0.25 wt % of the WC powder prior to molding the powder into a preform ceramic body.

Binding the attrited WC powder with wax aids in molding the material into a preform ceramic body that can be densified using any of a variety of densification techniques such as pressureless or low pressure sintering, hot pressing, hot isostatic pressing and rapid omnidirectional compaction. Densification is preferably accomplished by hot isostatic pressing. It is also preferable that the *in situ* debinding of the preform ceramic body is accomplished by heating the preform ceramic body, which is under a pressure of inert gas, at a rate of at least about 3.5° C per min to at least about 280° C and held at this temperature for at least about 45 min; and then increasing the temperature at a rate of at least about 1.5° C per minute to at least about 380° C and held at this temperature for at least about 45 minute; and then increasing the temperature at a rate of at least about 6° C per min to at least about 480° C and maintained at this temperature for at least about 3 min. Inert gas may be a pure inert gas or a mixture of inert gases selected from nitrogen, argon, helium, neon, krypton, and xenon.

*In situ* debinding of the preform ceramic body may be accomplished by increasing the temperature of the preform ceramic body in a controlled manner. For example, heating the preform ceramic body at a rate of 3.75° C per min to 300° C and maintaining this temperature for 1-h before increasing the temperature to 400° C at a rate of 2° C per min. Further, the preform ceramic body may be maintained at 400° C for 1-h before increasing the temperature to 500° C at a rate of 8° C per min. It is preferable that debinding and sintering the ceramic body is performed in a single cycle.

Sintering the preform ceramic body may be accomplished by placing the debinded preform ceramic body under vacuum and then controlling the temperature. For example, a vacuum may be applied to the preform ceramic body and the temperature increased at a rate of at least about 6° C per minute to at least about 1580° C and maintained at this temperature for at least about 45 min. The sintering process may be completed by releasing the vacuum and applying a pressure of inert gas to the ceramic body. For example, at least about 28 KSI inert gas pressure can be applied and held for at least about 45 min. Inert gas may be a pure inert gas or a

mixture of inert gases selected from nitrogen, argon, helium, neon, krypton, and xenon. It is preferred that debinding and sintering be performed in a single cycle.

The densified WC body produced by this method has a transverse rupture strength of 300,000 psi, a Rockwell A-scale hardness of up to 96 at 20° C and a Rockwell A-scale hardness of greater than 90 at 800° C. A densified ceramic body with a transverse rupture strength between about 300,000 psi and about 590,000 psi is suitable. Preferably, the densified ceramic body has a transverse rupture strength of at least about 325,000 psi, a Rockwell A-scale hardness of between about 94 and about 96 at 20° C and a Rockwell A-scale hardness of greater than 90 at 800° C.

The average WC particle size in the densified ceramic body is less than 1  $\mu\text{m}$ . A WC particle size between about 0.001  $\mu\text{m}$  and about 0.6  $\mu\text{m}$  is suitable. A WC particle size between about 0.1  $\mu\text{m}$  and about 0.45  $\mu\text{m}$  is preferred. Further, a ceramic body with a WC-bound carbon content of between about 5.5 wt % and 6.09 wt% is preferred. A substoichiometric WC-bound carbon content of between about 5.9 wt% and 5.98 wt% is most preferred. A stoichiometric carbon content is 6.13 wt%.

A densified ceramic body that is shaped as a cutting tool is preferred. A cutting tool with chip control is more preferred. The present invention may be utilized with a variety of insert chip control designs, such as those shown in U.S. Pat. Nos. 5,141,367; 4,318,645; 4,340,324; 4,247,232; 4,087,193; 4,056,871 and 3,383,748 and each fully incorporated herein by reference.

#### EXAMPLE 1

Mach 600 WC powder (Alldyne Powder Technology, West Huntsville, AL, USA) was processed to 0.41- $\mu\text{m}$  average particle size by repeated milling and spray-drying as follows. Mach 600 WC powder (lot #63794) having an average grain size of 0.8- $\mu\text{m}$  to 1.1- $\mu\text{m}$  and a vanadium carbide (VC) content of 0.33 wt % was ball-milled with n-heptane for approximately 70-h. The milling mixture was spray-dried and the attrited powder was recovered. The milling and spray-drying process was repeated as before. After a third cycle of milling, paraffin wax (2 wt %) and beeswax (0.25 wt %) were added during drying of the attrited WC powder to bind the attrited WC powder together. This powder also contained 0.47 wt % cobalt, 0.06 wt % Cr, and 0.03 wt % Fe.

A preform ceramic body was made by cold-dressing the attrited WC powder in steel tooling at 24,000 psi to provide a preform ceramic body having a size of 0.773 inch ("in.") by 0.773 in. by 0.320 in. and having 52.6 wt % of the theoretical density. The preform ceramic body was placed on a layer of coarse WC crystals in a carbon crucible and thermally processed in an AIP sinter vacuum 1800C/30KSI HIP furnace (American Isostatic Presses, Inc., Columbus, Ohio, USA).

*In situ* debinding of the preform ceramic body was accomplished with slight partial pressure of flowing nitrogen gas as follows. The preform ceramic body was heated under nitrogen at a rate of 3.75° C per min to 300° C. This temperature was maintained for 1-h before increasing the temperature to 400° C at a rate of 2° C per min. The preform ceramic body was maintained at 400° C for 1-h before increasing the temperature to 500° C at a rate of 8° C per min. This temperature was maintained for 5 min before sintering the part by pulling a hard vacuum and then increasing the temperature to 1600° C at a rate of 8° C per min. The preform ceramic body was sintered at 1600° C for 1h and then 30KSI nitrogen gas pressure was applied and held for 1h. The pressure was then released and the part recovered after air-cooling.

Physical property testing of the 0.638 in. by 0.638 in. by 0.266 in. part provided the following results:

Density: 15.6 g/cc [98.9 wt % of theoretical density based on pure WC (15.77 g/cc)<sup>a</sup>]

Hardness (Rockwell A): 95.7

Hardness, Vickers (1 kg load, 15 second dwell): 2588 kg/mm<sup>2</sup>

Carbon: 5.99 wt %

Mean Transverse rupture strength: >392,000 psi (n=2)

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<sup>a</sup> Smitbell's Metals Reference Book, 6<sup>th</sup> Ed., pg. 23-1 (1983).

## EXAMPLE 2

Densified polycrystalline tungsten carbide-containing ceramic bars were manufactured by the methods of the present invention using either Mach 400 ("material type-A"; Alldyne Powder Technology, West Huntsville, AL, USA) or Mach 600 ("material type-B"; Alldyne Powder Technology, West Huntsville, AL, USA). The transverse rupture strengths observed for material type-A and material type-B are summarized below in Table 1. Data are the mean  $\pm$  standard deviation of up to six determinations in each trial.

As shown in Table 1, the mean transverse rupture strengths of the ceramic bars exceeded 300,000 psi. There did not appear to be a significant difference in mean transverse rupture strength of ceramic bars produced using material type-A compared to the strength of ceramic bars produced using material type-B.

**Table 1. TRAVERSE RUPTURE STRENGTH TESTS**

Carmet		Carmet	
<b>Mach 600</b>		<b>Mach 400</b>	
<b>set #53228</b>	<b>TRS value (psi)</b>	<b>set #53229</b>	<b>TRS value (psi)</b>
bar 1	502,000	bar 1	170,000
bar 2	394,000	bar 2	99,000
bar 3	484,000	bar 3	244,000
		bar 4	247,000
average	<b>460,000</b>	average	<b>190,000</b>
s.d. +/-	<b>47,244</b>	s.d. +/-	<b>60,922</b>

Carmet		Carmet	
<b>Mach 600</b>		<b>Mach 400</b>	
<b>set #53711</b>	<b>TRS value (psi)</b>	<b>set #53709</b>	<b>TRS value (psi)</b>
bar 1	342,000	bar 1	359,000
bar 2	523,000	bar 2	418,000
bar 3	182,000	bar 3	439,000
bar 4	248,000	bar 4	459,000
Average s.d. +/-	<b>323,750</b> <b>128,321</b>	average s.d. +/-	<b>418,750</b> <b>37,419</b>
Osram		Osram	
<b>Mach 600</b>		<b>Mach 400</b>	
<b>set #53711</b>	<b>TRS value (psi)</b>	<b>set #53709</b>	<b>TRS value (psi)</b>
bar 1	449,000	bar 1	161,000
bar 2	590,000	bar 2	423,000
bar 3	263,000	bar 3	429,000
		bar 4	506,000
		bar 5	520,000
		bar 6	505,000
average s.d. +/-	<b>434,000</b> <b>133,918</b>	average s.d. +/-	<b>424,000</b> <b>123,623</b>

## EQUIVALENTS

Although particular embodiments have been disclosed herein in detail, this has been done by way of example for purposes of illustration only, and is not intended to be limiting with respect to the scope of the appended claims, which follow. In particular, it is contemplated by the inventors that various substitutions, alterations, and modifications may be made to the invention without departing from the spirit and scope of the invention as defined by the claims. The choice of WC starting material, binder composition, and inert gas type are believed to be a matter of routine for a person of ordinary skill in the art with knowledge of the embodiments described herein. Other aspects, advantages, and modifications are considered to be within the scope of the following claims.